NATURAL VARIATIONS OF ^{13}C ABUNDANCE IN COAL AND BITUMEN AS A TOOL TO MONITOR CO-PROCESSING

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INTRODUCTION

The use of coal to facilitate the generation of transportation grade fuel from bitumen, heavy oil or petroleum resids is a topic of continuing research.[1-3] In order to optimize the upgrading process one needs to know in what proportion each feedstock contributes to each product fraction. Conventional analytical methods are neither able to distinguish the contribution from either feedstock in the synthetic products, nor measure the subtle changes in product character in response to differing process conditions.

The inherent difference in the $^{13}C/^{12}C$ ratio between most coals and bitumen can be utilized as an isotopic tracer to assess the efficacy of co-processing. For example Vesta coal and Athabasca bitumen have sufficiently distinct $^{13}C/^{12}C$ ratios[4] that the measured $^{13}C/^{12}C$ of any product will accurately reflect the proportion of feed incorporated into the product. From the elemental analysis and the $^{13}C/^{12}C$ ratio of the feedstock and products one can calculate the amount of carbon derived from coal (CDC) in each product fraction.[4-5] Analogously the amount of bitumen derived carbon (BDC) can also be independently calculated. In this study the natural variation in ^{13}C concentration was utilized as an isotopic tracer to evaluate co-processing efficiency of a one litre stirred autoclave under differing process conditions. Process variables examined were coal concentration, several iron based catalysts (Fe_2O_3; Fe_2O_3 impregnated with TiO_2, SnO_2, or ZnO and a sludge obtained from a nickel refinery) and temperature.

EXPERIMENTAL PROCEDURE

Coal and bitumen with or without catalyst (3 wt% of Fe, based on daf. coal) were placed in a one litre magnadrive stirred autoclave equipped with an internal cooling coil. The autoclave was pressurized with H_2 (8.6 MPa. ambient temperature) and heated at 8°C per minute to the reaction temperature. The slurry was reacted at operational temperature (±1°C) for 45 minutes. Dried Vesta subbituminous coal (100 mesh) and the +350°C fraction of Athabasca bitumen were used as feeds. The major component fractions of Athabasca bitumen are shown in table 1 and the elemental and isotopic analyses are listed in table 2. Iron based catalysts were prepared by co-precipitation (atomic ratio of 1:1) as described by Tanabe *et al.* [6] The sludge was obtained from Sheritt Gordon's Fort Saskatchewan nickel refining plant (Fe_2O_3 74.1 wt%; Ni 19200 ppm., Co 3580 ppm., Mo 169 ppm.).

Table 1. Component Distribution of Bitumen (+350°C)

Fraction	Wt% Carbon
Distillate	14.9
Maltene	61.5
Asphaltene	23.6
Residue	0.0

Table 2. Elemental Analyses (wt%) of Vesta Coal and Athabasca Bitumen (+350°C)

Fraction	Coal	Bitumen
Carbon	71.6	82.4
Hydrogen	5.0	10.1
Nitrogen	1.7	0.5
Sulphur	1.0	4.9
Ash	17.0	0.7
Moisture	0.7	0.0
$\delta^{13}C$	-26.35	-30.46

† Values expressed in terms of PDB[7]

$\delta^{13}C$ of NBS 22 is -29.81 parts per thousand (ppt.) with respect to PDB.

In experiments involving changes in coal concentration 125 grams of stripped Athabasca bitumen (-350°C fraction removed by distillation) was co-processed with 0, 8, 15, 30 and 60 grams of vacuum dried Vesta subbituminous coal at an operational temperature of 430°C. A second set of autoclave runs was performed in which 125 gram aliquots of stripped bitumen were co-processed with 0,10, and 18 grams of Vesta coal. After reaction, the -300°C fraction was directly removed from the autoclave and trapped by condensation in an ice water trap, distilled to - 177°C then characterized using GC-MS. The influence of iron based catalyst upon coal solubilization was the second process variable examined. Coal (60 grams), stripped bitumen (125 grams), and various catalysts (no added catalyst, Fe_2O_3, Fe_2O_3/TiO_2, Fe_2O_3/SnO_2, Fe_2O_3/ZnO or nickel sludge) were reacted at 430°C. The third process variable examined was the influence of temperature upon co-processing. Three autoclave runs were performed in which 125 grams of stripped Athabasca bitumen were reacted with 60 grams of Vesta coal and Fe_2O_3 catalyst (3 wt% of Fe based on daf. coal weight) at 415°C, 430°C and 445°C.

The following fractions were isolated from the co-processed material: distillate (-524°C), maltene (n-pentane soluble), asphaltene (n-pentane insoluble - toluene soluble), and residue (toluene insoluble). Each product's elemental composition and $^{13}C/^{12}C$ ratio was measured.[4] Product gases were collected and analysed by GC. All the $^{13}C/^{12}C$ ratios were expressed in terms of the $\delta^{13}C$ notation of Craig[7] equation 1:

1) $$\delta^{13}C = \left(\frac{(^{13}C/^{12}C)_{sample} - (^{13}C/^{12}C)_{ref.}}{(^{13}C/^{12}C)_{ref.}} \right) X\ 1000$$

RESULTS AND DISCUSSION

Mass Balance Calculation

Contrast between the $^{13}C/^{12}C$ ratio of coal and bitumen may be utilized as a natural isotopic tracer to monitor coal or bitumen incorporation into synthetic product fractions. A two end member mixing model [8] can be algebraically derived to calculate the make up of the co-processed products, equation 2.

$$2)\ \%\ \text{COAL INCORPORATION} = \left(1 - \frac{\delta^{13}C_{prod} - \delta^{13}C_{coal}}{\delta^{13}C_{bit} - \delta^{13}C_{coal}}\right) \times 100\ \%$$

Two hydroprocessing experiments were performed using only bitumen in order to examine whether any isotopic shift would occur due to processing. Bitumen (125 grams) was processed at 430°C and bitumen (125 grams with 3 wt% Fe_2O_3) was processed at 445°C. Distillate (200°C to 524°C), maltene, asphaltene and residue fractions were found to be enriched (0.16, 0.37, 0.31 and 1.12 ppt. respectively) in ^{13}C relative to unprocessed bitumen fractions.[4] The naptha fraction was enriched in ^{12}C, (table 3). Such measurements serve as blanks and need to be substituted for $\delta^{13}C_{bit}$ in equation 2. In this study the calculated yields of carbon summed over all the fractions is within ±2% of the weight of the original charge.

Table 3: Isotopic Ratio of the Naptha Fraction (-177°C)

0 grams coal	-31.14 ppt.
10 grams coal	-30.99 ppt.
18 grams coal	-30.95 ppt.

† Values expressed in terms of PDB[7]

$\delta^{13}C$ of NBS 22 is -29.81 ppt. with respect to PDB.

Formation of crack gases enriches the residues in ^{13}C but the ^{12}C enrichment in the naptha is enigmatic. Two pathways for ^{12}C enrichment are possible; that large moieties have isotopic heterogeneity, or alternatively that the ^{12}C enrichment may result from a thermal process. Athabasca bitumen has been biodegraded to the stage where many of the original components, i.e. (alkanes and steranes) found in crude oils are no longer present.[9] However C_{27} to C_{29} steranes are released from the asphaltene fraction of Athabasca bitumen by hydropyrolysis[10] suggesting that the asphaltene fraction of bitumen may have incorporated alkanes from the original crude which are released upon thermal degradation. Recent work by Cyr *et al.* [11] indicates that in the highest molecular weight fraction (MW 16900) of Athabasca bitumen the aromatic core of the asphaltene is surrounded by alkyl chains with a mean length of 12. In nondegraded crude oil the alkane fraction is isotopically enriched in ^{12}C relative to the whole crude, while the cycloparaffin and aromatic fraction are relatively uniform.[12] These observations suggest that the observed ^{12}C enrichment of naptha may result from thermal degradation of moieties which have incorporated a portion of the original alkane fraction.

Alternatively, selective enrichment of a low molecular weight product fraction in ^{12}C by C-C bond scission is known to occur.[13-15] Pyrolysis of n-$C_{18}H_{38}$ at 500°C for one hour produced methane enriched in ^{12}C relative to the source by 15 ppt. The C_2 to C_4 gases showed similar but less pronounced enrichment with Sackett[15] suggesting that for C_2,C_3 and C_4 the isotope shift was 1/2,1/3 and 1/4 that of methane respectively.

Effect of Variations of Coal-Bitumen Ratio

Varying amounts of coal were co-processed with bitumen. Coal and bitumen incorporation into a product fraction has been calculated and plotted against the weight% of coal in the slurry, (figures 1,2). Co-processing experiments utilizing coal to bitumen ratios less than 15 wt%, exhibit a noticeable increase in distillate yield (14% to 17%) over and above distillate yields obtained by hydrotreatment of bitumen alone, (figure 1). Graphically there appears to be an antithetic correlation between bitumen-derived distillate and bitumen-derived maltene products. Increased distillate yield corresponds with a decrease in in the bitumen-derived maltene fraction. The shift to a more positive $\delta^{13}C$ value with increasing coal concentration, (table 3), indicates that coal is incorporated into the -177°C naptha fraction. For coal concentrations greater than 8 wt% the BDC incorporated into the maltenes are in excess of the maltene yields obtained from processing of bitumen alone. Increase in the maltene's BDC corresponds with a decrease in the BDC present in the asphaltene fraction. With increasing coal concentration, bitumen's incorporation into the asphaltene fraction decreases . Graphically it is more pronounced for low coal concentrations, (figure 1). Slurry compositions of 8 to 26 wt% coal show only a slight decrease in bitumen incorporation into asphaltenes over the entire range. The isotopically determined BDC yield of the distillate, maltene and asphaltene fractions suggest that the increase in distillate yields for coal-bitumen ratios of 4% to 8% is derived from the thermal degradation of the asphaltene and maltene fractions. The proportion of distillate derived solely from bitumen shows no appreciable change in yield for coal concentration in excess of 15 wt%, (figure 1). Higher coal concentration, however appear to enhance asphaltene conversion to maltene and residue fractions. The increase in bitumen's incorporation into residue parallels a measured increase in coal incorporation into residue, (figure 2). The sharp increase in residue is in part due to polymerization reactions (as evidenced by the increase in the bitumen-derived component of the residue), and in part by coal saturation in the slurry (as evidenced by the three fold increase in the coal-derived residue).

With increasing coal concentration, coal's contribution to each product fraction increases. Calculated yields of distillate (-524°C) solely derived from coal are observed to increase in near linear fashion with coal concentration, (figure 2). Incorporation of coal derived carbon (CDC) into the maltene fraction appears to be largely independent of coal concentration. For coal concentrations of 0 wt% to 15 wt%, a large relative increase in the coal derived proportion of the asphaltene exists. For concentrations in excess of 15 wt%, the amount of coal-derived asphaltenes appear to level off.

The naptha fraction recovered from three co-processing experiments for which 0,10 and 18 grams of Vesta coal were reacted with 137,126 or 126 grams of stripped bitumen was characterized using GC-(P(O)NA column) and GC-MS by means of retention times and library search of compounds. We have now identified, by means of GC-MS, in the naptha fraction of the 10 grams coal co-processing experiment , oxygen and sulphur bearing hydrocarbons; 2-3 dimethlythiophene, 2-4 dimethlythiophene, 2-3-4 trimethlythiophene, 2-3-5 trimethlythiophene, dimethylphenol and methylbenzothiophene.

Effect of Iron Based Catalyst

The effect of select metal oxides catalyst upon coal solubilization was the next process variable examined. The different catalysts affect the make-up of the synthetic liquids, (table 4). In all experiments the weight of feedstocks co-processed was held constant, 60 grams Vesta coal (35.4 grams carbon) and 125 grams of stripped Athabasca bitumen (102.3 grams carbon).

Table 4: Effect of Iron Based Catalyst (CDC, BDC* in grams)

Fraction	Blank		Fe_2O_3		Fe_2O_3/TiO_2		Fe_2O_3/SnO_2		Fe_2O_3/ZnO		Sludge	
	CDC	BDC	CDC	BDC	CDC	BDC	CDC	BDC	CDC	BDC	CDC	BDC
Distillate	7.3	52.7	6.7	46.1	6.5	46.1	7.7	46.1	8.8	54.2	7.6	49.6
Maltene	2.4	22.7	4.0	40.8	2.4	43.7	3.2	44.1	2.8	31.8	2.1	41.2
Asphaltene	9.7	9.5	17.6	11.8	18.7	11.6	13.5	8.7	12.2	11.3	16.5	10.4
Residue	13.5	5.8	5.7	0.2	6.7	0.1	10.4	1.8	10.5	2.2	7.6	0.8
Gas**	2.1	4.4	1.5	4.3	1.3	4.3	1.2	4.3	1.6	4.3	1.0	4.3
% Yield***	98.9	98.1	100.3	100.9	100.6	103.4	101.7	102.6	101.4	101.5	98.3	103.9

* Feeds: 60 g of coal (35.4 g carbon), 125 g of bitumen (102.3 g carbon)

** From GC analysis

*** Based on carbon in the feed

The contribution of both coal-derived carbon (CDC) and bitumen derived carbon (BDC) as calculated from $\delta^{13}C$ mass balance are listed for each product fraction. Isotopically calculated coal and bitumen contribution to the product fraction agree within 98 to 103% of the initial feedstock charge, (table 4).

Distribution of the CDC in both catalyzed and catalyst free experiments for the distillate and maltene fractions ranged from 6.5 to 8.8 grams. and 2.1 to 4.0 grams respectively. These results suggest that CDC incorporation into the maltene and distillate fractions may be largely independent of catalyst. Catalyst showed varying abilities to convert coal to asphaltene. Fe_2O_3 alone or Fe_2O_3/TiO_2 or sludge converted coal more effectively than did Fe_2O_3/SnO_2 to Fe_2O_3/ZnO; 16.5 to 17.6 grams for the former, 12.2 to 13.5 grams for the latter. For bitumen upgrading, large differences in the BDC incorporation into the residue exists. Feedstock bitumen, (table 2) contains negligible toluene insoluble material (residue), so BDC incorporation into the residue fraction must be due to coking. The blank run (no added catalyst) produces both a high coke yield (5.8 grams) and a high distillate yield (52.9 grams). Addition of catalyst strongly inhibited the formation of coke, 0.1 to 0.2 grams with Fe_2O_3 alone or with Fe_2O_3/TiO_2, 0.8 grams with sludge and 1.8 grams to 2.2 grams with Fe_2O_3/SnO_2 or Fe_2O_3/ZnO. Bitumen incorporation into residue appears to be closely related to distillate yield for experiments with added catalyst. The higher the residue yield, the more distillate obtained. Addition of Fe_2O_3/ZnO substantially increased distillate yield (54.2 grams), increased coke yields relative to other catalysts and decreased BDC incorporated into maltene fraction.

Effect of Temperature

Coke inhibition by Fe_2O_3 catalyst upon bitumen upgrading was investigated at three different temperatures, 415°C, 430°C and 445°C. The contribution of CDC and BDC to each product fraction is presented in (table 5). An initial charge of 60 grams of Vesta coal (35.4 grams carbon) and 125 grams of stripped Athabasca bitumen (102.3 grams) were used in all experiments.

Table 5: Effect of Temperature (BDC* and CDC in grams)

	(415°C)		(430°C)		(445°C)	
	CDC	BDC	CDC	BDC	CDC	BDC
Distillate	5.9	37.5	6.7	46.1	11.1	60.4
Maltene	2.5	52.2	4.0	40.8	3.5	18.9
Asphaltene	11.7	13.7	17.6	11.8	13.8	10.8
Residue	12.3	0.1	5.7	0.2	7.2	2.1
Gas**	-	3.6	1.5	4.3	3.0	3.9
% Yield***	90.3	104.5	100.3	100.9	102.4	92.0

* Feeds: 60 g of coal (35.4 g carbon),
126 g of bitumen (103.1 g carbon),
3 wt% Fe_2O_3 (based on daf coal wt.)

** From GC analysis

*** Based on feed carbon

Increasing operational temperatures from 415°C to 430°C increased coal incorporation into the maltene and asphaltene fractions (2.5 to 4.0 grams and 11.7 to 17.6 grams respectively), at the expense of the residue (decreased from 12.3 to 5.7 grams). Little change is observed in the coal derived distillate. At 415°C a large proportion of coal remains unreacted, 12.3 grams of coal derived residue out of an initial coal charge of 35.4 grams. Yields of BDC incorporated into distillate fraction increases with increasing temperature (37.5 to 46.1 grams) while bitumen contribution to the maltene and asphaltene fraction decreased (52.2 to 40.8 grams and 13.7 to 11.8 grams respectively).

Co-processing of bitumen and coal at 445°C generated significantly more distillate, but also more insoluble material. Coal derived distillate increased from 6.7 to 10.4 grams. Whereas coal incorporation into the residue fraction increased from 5.7 to 9.4 grams. The increase in distillate and residue was at the expense of a twofold decrease in CDC in the maltene and asphaltene fractions (4.0 to 1.4 grams and 17.6 to 9.6 grams respectively). With co-processing at 445°C an increase in bitumen's incorporation into distillate was also observed (46.1 to 60.4 grams). Coke formation in terms of insoluble matter (residue) sharply increased from .2 grams (430°C) to 2.2 grams (445°C). Increased distillate and residue yields correspond with a sharp decrease in maltene (40.8 to 18.9 grams). The asphaltene fraction remained nearly constant, 11.8 grams at 430°C to 10.8 grams at 445°C.

CONCLUSIONS

A stable isotope mass balance techniques was used to investigate the efficiency of single stage coal-bitumen co-processing for the solubilization of coal. The results indicate that during co-processing:

1) Uncatalyzed co-processing of coal-bitumen mixtures comprising of 5 to 10 wt% coal enhance bitumen conversion to distillate by 14 to 17%. Concordantly the bitumen derived component of the asphaltene fraction decreases from 32 to 49% with respect to yields obtained in the hydrotreatment of bitumen alone. Coal concentrations of 15 to 26 wt% result in no appreciable increases in distillate over processing of bitumen
2) Increase in coal concentration from 0 to 26 wt% results in a progressive increase in coal incorporation into the distillate, maltene, asphaltene and residue fractions; and that a change in coal concentration from 15 to 26 wt% results in a threefold increase in coal derived residue.
3) In the naptha fraction of co-processing experiment (5 wt% coal) dimethyl thiophenes, trimethyl thiophenes, dimethyl phenol and methyl benzothiophene have been detected using GC-MS. No contrast exists in compound types as determined by GC between coal-bitumen and bitumen only runs. Isotopic mass balance calculations indicate that coal is incorporated into these fractions.
4) Coal incorporation in the distillate and maltene fractions appears to be independent of the iron based catalyst used.
5) Iron based catalyst strongly inhibits coke formation from bitumen and increases coal solubilization into asphaltene fractions.
6) Fe_2O_3/ZnO and Fe_2O_3/SnO_2 increased residue yield from bitumen with respect to Fe_2O_3, Fe_2O_3/TiO_2, and nickel sludge.
7) Sludge from nickel refining can be used as an effective coal solubilization catalyst.
8) Autoclave reaction temperature of 445°C increased bitumen's conversion to distillate by 31% with respect to distillate yield obtained in co-processing at a temperature of 430°C. However a sharp increase in bitumen coking is observed in experiments processed at 445°C.

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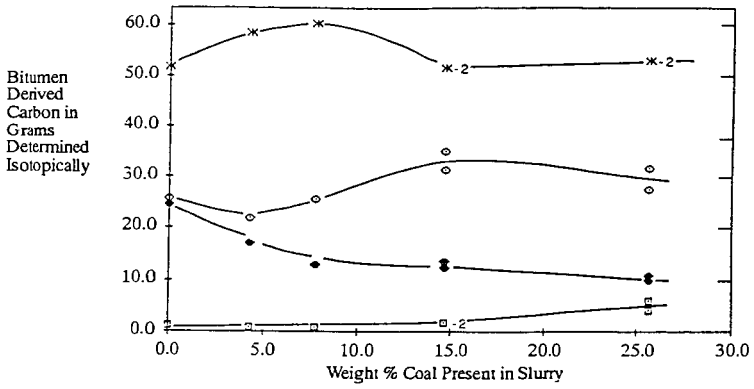

Figure 1 Variation in the isotopically determined amount of bitumen derived carbon incorporated into each synthetic liquid as a function of coal concentration in the slurry. Symbols: ⁎ - Distillate; ◇ - Maltene; ◆ - Asphaltene; ▫ - Residue.

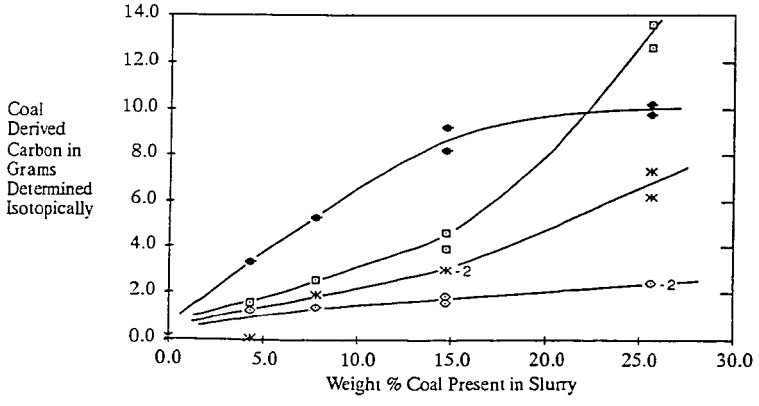

Figure 2 Variation in the isotopically determined amount of coal derived carbon incorporated into each synthetic liquid. Symbols: ⁎ - Distillate; ◇ - Maltene; ◆ - Asphaltene; ▫ - Residue.